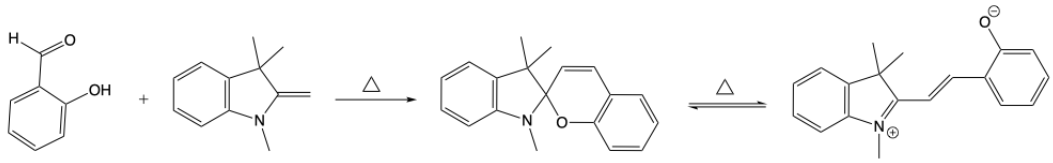
Exp 8: Functional Organic Materials and Molecular Modeling

Preparation of 1′,3′,3′-Trimethylspiro(chromene-2,2′-indoline)

Purpose

The goal of the experiment is to prepare 1′,3′,3′-trimethylspiro(chromene-2,2′-indoline and explore the thermochromism properties. The crystalline product will be analyzed with X-ray crystallography and NMR spectroscopy.



Textbook reference

Brown, Iverson, Anslyn, & Foote, Section 19.5.

Learning Objectives

Perform a synthesis.

Purify a product by recrystallization.

Use a melting point determination to analyze the product of a reaction.

Use IR spectroscopy to confirm the product of the reaction.

Analyze x-ray crystallographic data of the product.

Equipment

- Reflux set up
- Büchner funnel with a vacuum filtration setup
- Rotary evaporator
- Steam bath
- Pyrex test tube
- Boiling stone
- Aluminum block heater
- 1-dram vial with a small hole in the cap
- 42 MHz SpinSolve NMR and tubes

Chemicals

- 1,3,3-Trimethyl-2-methyleneindoline
- Salicylaldehyde
- Absolute ethanol
- Reagent grade
- acetone
- 90% Ethanol
- Diphenyl ether
- $CDCl_3$

Procedure

Part 1: Synthesis

1. Prepare a solution of 3.3 g of 1,3,3-trimethyl-2-methyleneindoline and 2.1 g of salicylaldehyde in 15 mL of absolute ethanol.

2. Heat the reaction mixture at reflux for 1 hour.

3. Filter the hot mixture with vacuum filtration and wash the filtered solid with a small amount of cold ethanol (5 mL).

4. Recrystallize the crude minor product (solid material on the filter paper) with acetone.

5. Obtain a mass of the minor product and determine the yield.

6. Perform a melting point determination of the minor product and record the value.

7. Evaporate the combined filtrate/alcohol wash using a rotary evaporator.

8. Recrystallize the resulting crude major product from 90% ethanol using a steam bath. Be careful not to melt the product.

9. Wash the crystals with cold absolute ethanol to reduce the amount of pigment in the sample.

10. Obtain a mass of the major product and determine the yield.

11. Perform a melting point determination of the major product and record the value.

Part 2: Thermochromism

12. Introduce a sample of the major product (about 250 mg) into a Pyrex test tube and add 5 mL of diphenyl ether. The test tube should be no more than one quarter full.

13. Add a boiling stone and gently boil the mixture by contacting the tube to a heated aluminum block on a hotplate.

14. Record your observations.

Part 3: Crystal growing

15. Large crystals suitable for X-ray crystallography (see Part 5) can be grown by dissolving 10–20 mg of your major product in 1 mL of acetone in a 1 dram vial with a small hole in the cap.

16. Leave the solution to evaporate in your locker.

17. Record your observations.

Part 4: Analysis using NMR spectroscopy

18. Dissolve 25 mg of your purified product in 0.5 mL $CDCl_3$ and transfer to an NMR tube.

19. Use the 42 MHz SpinSolve NMR in the classroom to obtain NMR spectra for your isolated product as well as the 1,3,3-trimethyl-2-methyleneindoline starting material.

20. Assign the structures of your product from these spectra.

21. Include the spectra with your report.

Part 5: X-ray crystallography

22. Include crystal structures of major and minor products in your report. Crystallographic data can be obtained here: Xray Crystallographic Data.

23. Include a, b, c, and alpha, beta, gamma values for the unit cell of the structures (Some of these are not obvious, and a careful look into the Laue point group will explain what alpha, beta, and gamma should be for that group).

Report

1. Write a full curved-arrow mechanism for this reaction, including the thermochromic process.

2. How does the NMR of the product and starting material differ? Could you use one (or more) peaks to track the progress of your reaction by NMR spectroscopy?

3. The first solid isolated in this reaction is actually a minor product which arises from the reaction of a second molecule of 1,3,3-trimethyl-2-methyleneindoline with the major product shown above. Draw the structure of this minor product.

4. Briefly explain what thermochromism is.

5. Based on the outcome of the thermochromism experiment, deduce which of the structures should be lower in energy, and explain your reasoning.

6. Draw a diagram of a simple x-ray experiment. Be sure to include the x-ray source, the crystal and the diffraction patterns obtained.

7. Thermochromic materials can be used in write-read-erase-rewrite media. Using the product of this experiment, discuss how you could design a recording medium based thereupon.